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The study of the infrared and Raman spectra and determination of the thermodynamic functions of 4-cyanopyridine

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In continuation of our earlier study of the infrared and Raman spectra of substituted pyridines (Medhi 1977, 1982, 1983, 1984), the vibrational spectra of 4-cyanopyridine have been investigated in this communication. Spinner (1963) measured the infrared spectrum of the molecule in a very limited range. The infrared and simple Raman spectra of the melt or solution of 4-cyanopyridine were measured by Green and Harrison (1977) and a vibrational assignment based on comparison with that of benzonitrile (Green and Harrison 1976) was given. For the computation of the thermodynamic quantities of the molecule, an accurate knowledge of the fundamental frequencies is necessary. Assignments of the observed frequencies based on the state of polarization of the Raman lines and comparison with the assignments proposed for related molecules (Green *et al* 1963, Long and George 1963, Berezin and Elkin 1973, Long and Bailey 1963) are given in the present paper, and are compared with the previous assignments (Green and Harrison 1977). The ideal gas-state thermodynamic functions of the molecule on the basis of the present assignment have been calculated.

The polarization of the Raman lines was measured in the melt. The observed infrared frequencies and Raman shifts of 4-cyanopyridine together with their relative intensities and assignments are collected in Table 1. Table 2 lists the thermodynamic functions.

The molecule of 4-cyanopyridine belongs to C_{2v} point group symmetry, and its 30 normal vibrations divide into various species as :

$$11a_1 + 10b_2 + 3a_2 + 6b_1$$

According to the selection rule a_2 species is inactive in the infrared spectrum.

There appear only three frequencies below 400 cm^{-1} in the case of 4-cyanopyridine, whereas five fundamentals are expected in this region. Green and Harrison (1977) assigned the Raman lines at 172 cm^{-1} to the C – N in-plane bending

mode (b_2) and 376 cm^{-1} (present value) to a substituent-sensitive b_1 mode. In the case of pyridine and 4-methyl and 4-halogen substituted pyridines the frequency

Table 1. Vibrational frequencies and assignments for 4-cyanopyridine.

Infrared (cm^{-1})		Raman shift (cm^{-1})		Assignment
Thin film	Solution	Melt	Single crystal	
—	—	—	120 (s)	Lattice mode
—	—	—	130 (mw)	
149 (s)		145*	144 (s)	ν_1 (b_1), C–N out-of-plane deformation
170 (s)	–	172 (16) dp	190 (s)	ν_2 (b_1), 16b; ν_3 (b_2), 18b
368 (mw)	—	376 (1) dp	374 (w)	ν_4 (b_2), C–N in-plane deformation; ν_5 (a_2), 16a
	455 (mw)	455 (27) p	455 (mw)	ν_6 (a_1), 6a
		548 (3) dp	—	$\nu_2+\nu_4$ (A_2)
	563 (vs)	563 (6) dp	560 (ms)	ν_7 (b_1), 11
610	613 (w)	—	—	$\nu_1+\nu_6$ (B_1)
660	668 (w)	669 (11) dp	667 (ms)	ν_8 (b_2), 6b
726	711 (mw)	—	—	ν_9 (b_1), 4
751	—	748 (2) p	—	$2\times\nu_4$ (A_1)
775	—	775 (25) p	775 (ms)	ν_{10} (a_1), 12
827	824 (vs)	822 (1) dp	829 (w)	ν_{11} (b_1), 10b
	871 (w)	—	—	ν_{12} (a_2), 10a
	887 (w)	—	—	$\nu_4+\nu_9$ (A_1)
911	911 (vw)	—	—	ν_{13} (b_1), 5
929	934 (mw)	938 (2) p	—	$\nu_3+\nu_{10}$ (B_2)
970	965 (mw)	980 (h)	977 (w)	ν_{14} (a_2), 17a
987	991 (s)	990 (100) p	987 (s)	ν_{15} (a_1), 1
1035	1042 (w)	—	—	$\nu_4+\nu_8$ (A_1)
1080	1065 (ms)	1067 (3) p	1073 (w)	ν_{16} (a_1), 18a
	1078 (mw)	1092 (1) p		$\nu_2+\nu_{15}$ (A_1)
1107	1102 (mw)	1108 (1) p	—	ν_{17} (b_2), 15
		1125 (1) p	—	$2\times\nu_7$ (A_1)
1200	1194 (ms)	1193 (78) p	1192 (ms)	ν_{18} (a_1), 9a
	1208 (s)	—	1209 (h)	ν_{19} (b_2), 3
	1218 (ms)	—	—	$\nu_1+\nu_{16}$ (B_1)
1235	1226 (ms)	1233 (3) p	1235 (w)	ν_{20} (a_1), 13
1250	1245 (w)	—	—	$\nu_2+\nu_{16}$ (B_1)
1332	1323 (w)	1328 (2) dp	1335 (w)	ν_{21} (b_2), 14
1369	1354 (w)	—	—	$\nu_4+\nu_{15}$ (B_2)
1410	1407 (vs)	1407 (1) dp	1412 (w)	ν_{22} (B_2), 19b
1434	1428 (mw)	—	—	$\nu_4+\nu_{16}$ (B_2)
—	—	1462 (1) p	1463 (w)	$\nu_6+\nu_{15}$ (A_1)
1493	1487 (ms)	1488 (11) p	1494 (w)	ν_{23} (a_1), 19a

Table I. (Contd.)

Infrared (cm^{-1})		Raman shift (cm^{-1})		Assignment
Thin film	Solution	Melt	Single crystal	
1542	1552 (s)	1547 (1)	1542 (w)	ν_{24} (b_2), 8*b*
1588	1591 (vs)	1591 (33) p	1592 (ms)	ν_{25} (a_1), 8*a*
1615	1623 (w)	—	—	$\nu_9+\nu_{18}$ (B_2)
1716	1684 (mw)	—	—	$\nu_{11}+\nu_{12}$ (A_1)
1748	1750 (w)	—	—	$2\times\nu_{17}$ (A_1)
1797	1778 (w)	—	—	$\nu_{12}+\nu_{13}$ (B_2)
1856	1848 (w)	—	—	$\nu_{11}+\nu_{18}$ (B_2)
				$\nu_{13}+\nu_{14}$ (A_1)
1969	1939 (mw)	—	—	$\nu_6+\nu_{23}$ (A_1)
2045	2037 (w)	—	—	$\nu_9+\nu_{20}$ (B_1)
2071	2073 (w)	—	—	$\nu_{16}+\nu_{18}$ (A_1)
2153	2153 (w)	—	—	$\nu_9+\nu_{22}$ (A_1)
2187	2191 (w)	2185 (4) p	2177 (ms)	$\nu_7+\nu_{23}$ (B_1)
2240	2244 (ms)	2237 (60) p	2242 (s)	$\nu_{15}+\nu_{18}$ (A_1)
				ν_{26} (a_1), C N stretching
2312	2308 (w)	—	—	$\nu_{11}+\nu_{23}$ (B_1)
2408	2406 (w)	2415 (1) p	—	$\nu_{16}+\nu_{20}$ (A_1)
2724	2744 (w)	—	—	$\nu_{21}+\nu_{22}$ (A_1)
2780	2780 (w)	—	—	$\nu_{18}+\nu_{25}$ (A_1)
2888	2882 (mw)	—	2892 (w)	$\nu_{22}+\nu_{23}$ (B_2)
2918	2912 (w)	—	—	$\nu_{21}+\nu_{25}$ (B_2)
2982	2984 (w)	2967 (7) p	2974 (w)	$2\times\nu_{25}$ (A_1)
3022	3030 (mw)	3033 (12) dp	3027 (mw)	ν_{27} (b_2), 7*b*
3040	3052 (ms)	3052 (h)	3047 (ms)	ν_{28} (a_1), 20*a*
3076	3066 (ms)	3067 (99) p	3665 (ms)	ν_{29} (a_1), 2
3088	3082 (mw)	3091 (16) dp	3085 (w)	ν_{30} (b_2), 20*b*
3130	3142 (w)	—	3159 (w)	$\nu_{24}+\nu_{25}$ (B_2)
3200	—	3179 (6) p	—	$2\times\nu_{25}$ (A_1)
3416	3425 (w)	—	—	$\nu_4+\nu_{20}$ (B_2)
3530	—	—	—	$\nu_6+\nu_{29}$ (A_1)
3605	—	—	—	$\nu_7+\nu_{29}$ (B_1)
3684	—	—	—	$\nu_{11}+\nu_{27}$ (A_1)
3754	—	—	—	$\nu_{15}+\nu_{30}$ (A_1)

*Taken from Green and Harrison (1977). †Observed in pellet.

occuring in the range 375-390 cm^{-1} was assigned to the lowest pyridyl a_2 mode (Green *et al* 1963, Long and George 1963). Moreover, in acetonitrile the C–C ≡ N in-plane bending occurs at 380 cm^{-1} (Herzberg 1966). On the basis of these assignments it appears reasonable to assign the depolarized Raman shift at 376 cm^{-1} to the C–N bending mode (b_2). Similarly, the depolarized Raman shift at 172 cm^{-1} and the corresponding strong infrared band at 170 cm^{-1} are assigned

to both b_1 and substituent-sensitive b_2 modes. The latter mode was assigned by Green and Harrison (1977) to the depolarized Raman line at 548 cm^{-1} which appears to be quite high. The assignment of this mode (b_2) to a frequency near 300 cm^{-1} in methyl and halogen substituted pyridines (Green *et al* 1963, Long and George 1963) confirms the present assignment. The frequency 548 cm^{-1} can be explained as the sum band 172+376 = 548 (A_2). The Raman line at 938 cm^{-1} is

Table 2. Thermodynamic functions of 4-cyanopyridine*.

Temperature K	C_p° cal K^{-1} mol^{-1}	$\frac{(H^\circ - E_0^\circ)}{T}$ cal K^{-1} mol^{-1}	S° cal K^{-1} mol^{-1}	$-\frac{(F^\circ - E_0^\circ)}{T}$ cal K^{-1} mol^{-1}
200	18.74	12.57	70.35	57.78
250	22.17	14.15	74.89	60.75
273.1	23.80	14.89	76.93	62.04
298.1	22.56	15.72	79.09	63.38
300	25.68	15.78	79.25	63.47
400	32.30	19.10	87.56	68.47
500	37.87	22.31	95.39	73.08
600	42.39	25.30	102.70	77.41
700	46.06	28.01	109.50	81.52
800	49.09	30.46	115.90	85.42
900	51.63	32.68	121.80	89.14
1000	53.77	34.68	127.40	92.69
1100	55.59	36.50	132.60	96.08
1200	57.14	38.16	137.50	99.33
1300	58.47	39.67	142.10	102.40
1400	59.62	41.06	146.50	105.40
1500	60.61	42.33	150.60	108.30

*Ideal gas state at standard pressure of 1 atm.

observed to be polarized. So it cannot be assigned to an a_2 fundamental (Green and Harrison 1977). Instead, the very weak infrared band at 871 cm^{-1} appears to be a reasonable assignment for this a_2 mode.

Other alterations suggested are those in the assignments of the C–H in-plane bending modes of b_2 class. The strong infrared absorption at 1208 cm^{-1} and the moderately intense infrared absorption at 1102 cm^{-1} are selected for these two modes against the previous assignments (Green and Harrison 1977) of 1218 and 1078 cm^{-1} to these modes on the basis of intensity and similar assignments in the case of γ-picoline (Long and George 1963). A depolarized Raman line at 1407 cm^{-1} is now observed. It confirms the previous assignment of its infrared counterpart at 1407 cm^{-1} (present value) to the b_2 species. The assignment of the remaining fundamentals agrees with the previous assignment (Green and Harrison 1977).

Additional frequencies observed in the Raman and infrared spectra are explained as combination bands or overtones of the fundamental frequencies.

Ideal gas state thermodynamic quantities of 4-cyanopyridine have been calculated assuming a rigid rotator and harmonic oscillator approximation.

All the C–H stretching vibrations are well-resolved in the crystal spectra. No observable splitting in frequency has been observed in the crystalline state indicating that the crystal field interaction in the single crystal is weak. Moreover, the assignments of C–C ≡ N bending modes are tentative and yet to be confirmed by similar studies of $-CN^{15}$ substituted cyanopyridine.

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References

Berezin V I and Elkin M D 1973 *Opt. Spectrosc.* **34** 395
Green J H S and Harrison D J 1977 *Spectrochim. Acta* **33A** 75
1976 *Spectrochim. Acta* **32A** 1279
Green J H S, Kynaston W and Paisley H M 1963 *Spectrochim. Acta* **19** 549
Herzberg G 1966 *Infrared and Raman Spectra of Polyatomic Molecules* (Princeton : Van Nostrand) p 333
Long D A and George W O 1963 *Spectrochim. Acta* **19** 1777
Long D A and Bailey R T 1963 *Trans. Farad. Soc.* **59** 599
Medhi K C 1977 *Indian J. Phys.* **51A** 399
—1982 *Proc. Indian Acad. Sci.* (Chem. Sc.) **91** 137
—1983 *Bull. Chem. Soc. Japan* **56** 3486
—1984 *Bull. Chem. Soc. Japan* **57** 261
Spinner F 1963 *J Chem Soc.* 3860